Synthesis of α,β-Unsaturated Acylsilanes and an Unusual Thermal Reaction Involving a Siladiene

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Several α,β-unsaturated acylsilanes were prepared by coupling poly(silyllithium) reagents with acid chlorides. Thermolysis of the α,β-unsaturated acylsilane formed by coupling of $(Me_3Si)_3SiLi$ with $ClCOCH=CMe_2$ led to the isolation of $(Me_3Si)_2SiHC(OSiMe_3)=CHCMe_2-Si(SiMe_3)_3$, presumably as the result of rearrangement of the acylsilane to its isomeric siladiene, $(Me_3Si)_2Si=C(OSiMe_3)CH=CMe_2$, followed by the addition of $(Me_3Si)_3Si^•$ and hydrogen abstraction. The identity of the compound was confirmed by an X-ray crystal structure.

Following the success of silene stabilization by use of bulky substituents on the ends of the silicon−carbon double bond,[1,2] it appeared timely to attempt the preparation of a stable 1-sila-1,3-diene. Transient siladienes have been described by Weber[3] and by Conlin,[4] who measured the rate of electrocyclic ring closure of 1,1-dimethyl-1-sila-2-phenyl-1,3-butadiene to the isomeric silacyclobutene.

We proposed to prepare α,β-unsaturated acylsilanes by coupling of a poly(silyllithium) reagent with an α,β-unsaturated acid chloride: on photolysis, the resulting acylsilanes were expected to undergo the usual 1,3-shift of a trimethylsilyl group from silicon to oxygen,[1,2] as shown in Scheme 1. To avoid electrocyclic conversion of the siladiene to the isomeric silacyclobutene, it seemed desirable that the substituents R, R′, and R″ be as bulky as possible. Numerous relatively simple β,γ-unsaturated acylsilanes have been described.[5]

While poly(silylmetallic)s generally couple cleanly with simple acid chlorides to form acylsilanes, attempts to couple silyllithium reagents such as $(Me_3Si)_3SiLi$, Is-$(Me_3Si)_2SiLi$, and $Is_2(Me_3Si)SiLi$ (Is = 2,4,6-triisopropylphenyl), or the reagents formed by their reactions with CuI, with several α,β-unsaturated acid chlorides, such as $Ph_2C=CHCOCl$, $Me_3CCH=CHCOCl$, $Me_2C=CH-COCl$, or $Mes_2C=CHCOCl$, in THF−Et$_2$O at room temperature or −78 °C were found to be relatively unsuccessful. When the reactions were successful, low to modest yields of somewhat unstable oils were obtained. In other cases, instead of coupling, 1-electron transfer processes occurred between the initial reactants, leading to the formation of products of silyl and acyl radical hydrogen abstractions or self-couplings as shown in Scheme 1.

The α,β-unsaturated acylsilanes listed in Table 1 were somewhat unstable and decomposed during chromato-

Table 1. Products from Reactions of Silylmetallics with α,β-Unsaturated Acid Chlorides

product	yield (%)	^{29}Si central Si (ppm)	^{13}C C=O (ppm)
$(Me_3Si)_3SiCOCH=CPh_2$ (**1**)	47	−70.9	235.9
$(Me_3Si)_3SiCOCH=CMe_2$ (**2**)	83	−72.6	236.3
$(Me_3Si)_3SiCOCH=CHCMe_3$ (**3**)	*a*	−72.7	235.0
$Is(Me_3Si)_2SiCOCH=CMe_2$*b* (**4**)	35	−44.4	236.3
$Is(Me_3Si)_2SiCOCH=CPh_2$ (**5**)	17	−43.1	232.6

a Unstable, obtained in only about 80% purity. *b* Is = 2,4,6-triisopropylphenyl.

graphic purification or upon attempted distillation, so that pure samples for analysis were not obtained. They were characterized by mass spectrometry and by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, and each showed a ^1H =CH resonance in the range 6.35−6.47 ppm, a ^{13}C =CH resonance in the range 119−134 ppm, a C=O resonance in the range 232−236 ppm typical of a poly(silylacylsilane),[6] and a "central" silicon ^{29}Si resonance in the range of either −36 to −44 ppm (when Is was attached to the Si atom) or −70 to −73 ppm (for $(Me_3Si)_3Si$ systems), which is also typical.[6]

When the oils, which unquestionably contained mostly the desired α,β-unsaturated acylsilane, were subjected to photolysis using radiation of >360 nm, instead of the desired 1,3-trimethylsilyl shift from silicon to oxygen to form the siladiene occurring, for which there is ample precedent in simpler systems,[1,2] Norrish type 1 cleavage to radicals generally occurred, leading to the dimers of the silyl radicals formed, i.e., disilanes, and to products of the acyl radicals formed, which included aldehydes resulting from hydrogen abstraction or 1,2-dioxo compounds from acyl radical self-coupling. These processes are illustrated by the typical example shown in Scheme 2.

In an attempt to avoid radical formation, the acylsilane **2** was heated, which precedent suggested[2] might also lead to the desired α,β-unsaturated silene **6**. Instead, a product, **9**, was obtained in substantial yield, whose formation is best explained as arising as a result of two different reactions. In part the acylsilane **2** thermally rearranged to the desired α,β-unsaturated silene **6**, while another part underwent homolysis to the

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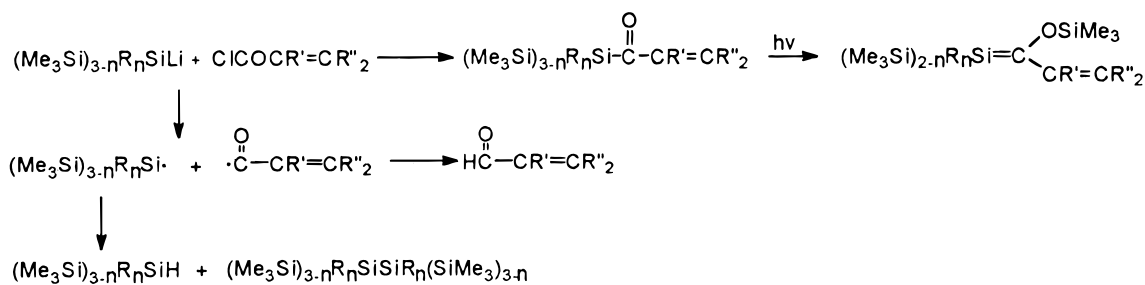(2) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982,** *104,* 5667.
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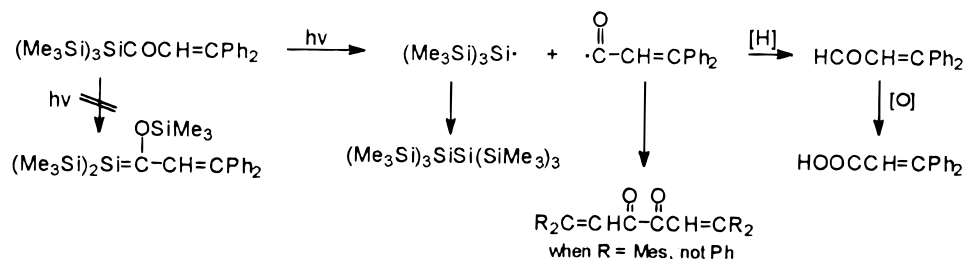(4) Conlin, R. T.; Zhang, S.; Namavari, M.; Bobbitt, K. L.; Fink, M. J. *Organometallics* **1989,** *8,* 571.
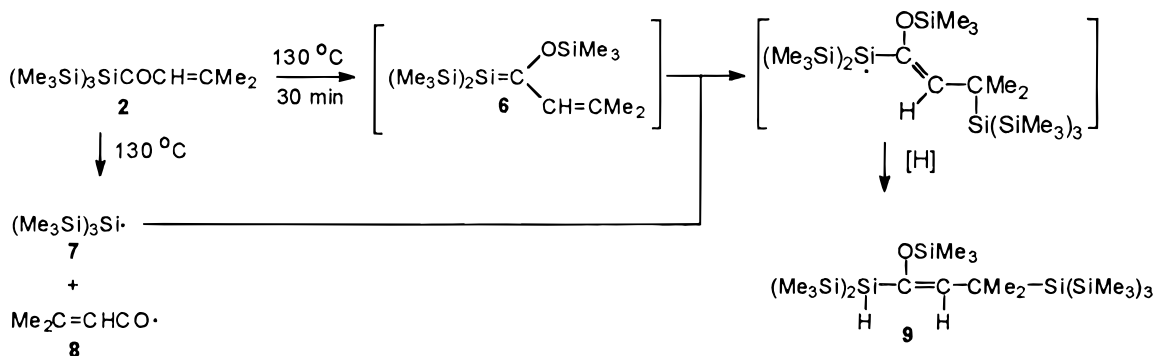(5) For a review, see: Bulman Page, P. C.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990,** *19,* 647.

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Scheme 1

$$(Me_3Si)_{3-n}R_nSiLi + ClCOCR'=CR''_2 \longrightarrow (Me_3Si)_{3-n}R_nSi-\overset{\overset{\displaystyle O}{\|}}{C}-CR'=CR''_2 \overset{h\nu}{\longrightarrow} (Me_3Si)_{2-n}R_nSi=C\overset{OSiMe_3}{\underset{CR'=CR''_2}{}}$$

$$(Me_3Si)_{3-n}R_nSi\cdot \; + \; \overset{\overset{\displaystyle O}{\|}}{\cdot C}-CR'=CR''_2 \longrightarrow H\overset{\overset{\displaystyle O}{\|}}{C}-CR'=CR''_2$$

$$(Me_3Si)_{3-n}R_nSiH \; + \; (Me_3Si)_{3-n}R_nSiSiR_n(SiMe_3)_{3-n}$$

Scheme 2

$$(Me_3Si)_3SiCOCH=CPh_2 \overset{h\nu}{\longrightarrow} (Me_3Si)_3Si\cdot \; + \; \overset{\overset{\displaystyle O}{\|}}{\cdot C}-CH=CPh_2 \overset{[H]}{\longrightarrow} HCOCH=CPh_2$$

$$h\nu \; \| \;$$

$$(Me_3Si)_2Si=\overset{OSiMe_3}{\underset{}{C}}-CH=CPh_2$$

$$(Me_3Si)_3SiSi(SiMe_3)_3$$

$$HOOCCH=CPh_2$$

$$R_2C=CH\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}CH=CR_2$$
when R = Mes, not Ph

Scheme 3

$$(Me_3Si)_3SiCOCH=CMe_2 \overset{130\,°C}{\underset{30\,min}{\longrightarrow}} \left[(Me_3Si)_2Si=C\overset{OSiMe_3}{\underset{CH=CMe_2}{}} \right] \longrightarrow \left[(Me_3Si)_2Si-\overset{OSiMe_3}{\underset{}{C}} \overset{}{\underset{H}{\underset{}{C}}}-C\overset{}{\underset{Si(SiMe_3)_3}{\underset{}{CMe_2}}} \right]$$

2   **6**

$$\downarrow 130\,°C$$

$$[H] \downarrow$$

$$(Me_3Si)_3Si\cdot$$
7

$$+$$

$$Me_2C=CHCO\cdot$$
8

$$(Me_3Si)_2Si-\overset{OSiMe_3}{\underset{H}{\underset{}{C}}}=\overset{}{\underset{H}{\underset{}{C}}}-CMe_2-Si(SiMe_3)_3$$
9

silyl radical **7** and the acyl radical **8**. Siladiene **6** then reacted with the silyl radical **7**, leading, via the adduct radical and hydrogen abstraction, to the product **9** for which an X-ray crystal structure was obtained. The reactions are summarized in Scheme 3. To the best of our knowledge, this sort of reaction, which is effectively a 1,4-hydrosilylation of a siladiene, has not been observed before. Its occurrence constitutes strong evidence of conjugation involving the Si=C and C=C bonds of the siladiene.

The Ortep diagram for the crystal structure of **9** is shown in Figure 1, confirming the structure proposed on the basis of the NMR spectroscopic data. The molecules had no unusual structural features. The data are given in the Experimental Section and supporting information.

The chemistry described indicates a lack of success to date in synthesizing a stable siladiene. The requisite highly hindered acylsilane starting materials, where it was hoped that bulky groups would inhibit the possible electrocyclic reaction of the siladiene leading to a silacyclobutene, were difficult to prepare, probably because of steric hindrance, which seriously affected the ease of coupling of the reagents. Other approaches are being investigated.

Experimental Section

All experiments were performed with oven-dried glassware under nitrogen by using standard inert-atmosphere and
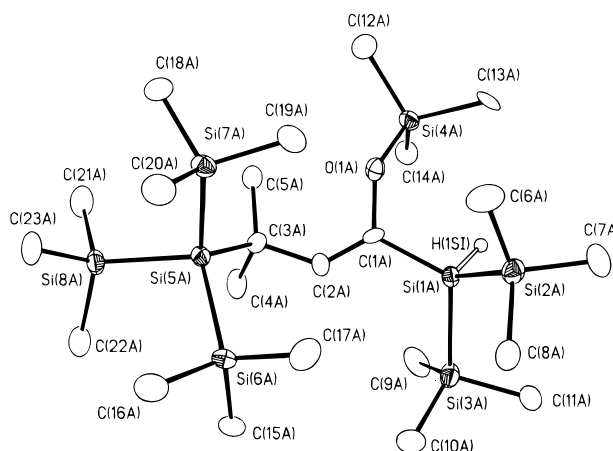

Figure 1.

vacuum-line techniques. All reaction solvents were dried and distilled prior to use: diethyl ether and tetrahydrofuran were dried over sodium benzophenone ketyl, hexanes were dried over a sodium–potassium alloy, and benzene was dried over lithium aluminum hydride. Photolyses were carried out at about 10 °C using three 100 W PAR 38 mercury spot lamps, whose output is mainly at 360 nm and longer wavelengths.

All ^{1}H NMR spectra were obtained on a Gemini 200 spectrometer, and a Varian XL400 machine was used to record ^{13}C and [29]Si spectra. The spectra were run in C_6D_6 unless otherwise specified. Where necessary, APT and DEPT pulse sequences were used in obtaining ^{13}C spectra to allow unam-

biguous assignment of signals. Most ^{29}Si spectra were obtained by using the DEPT pulse sequence.

All mass spectra were run on a VG 70-250S mass spectrometer operating in the electron impact (EI) mode for both low- and high-resolution mass spectra. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Melting points are uncorrected.

3,3-Diphenylacrylic Acid. Diphenylethylene was prepared following the known procedure[7] in 65% yield: ^{1}H NMR (CDCl$_3$) δ 5.39 (s, 2 H, CH$_2$=), 7.05−7.14 (m, 10 H, Ph); ^{13}C NMR (CDCl$_3$) δ 114.93 (CH$_2$=), 151.08 (Ph$_2$C=), 142.39 (Ph ipso), 128.49, 129.02, 129.14 (Ph CH). The acid was prepared, following the known procedure,[8] from oxalyl chloride and 1,1-diphenylethylene in 55% yield: mp 167 °C; ^{1}H NMR (CDCl$_3$) δ 6.34 (s, 1 H, =CH), 7.24−7.40 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 116.97 (CH=), 128.42, 128.90, 129.02, 129.77, 130.92 (Ph CH), 138.92, 141.34 (Ph ipso), 159.46 (Ph$_2$C=), 171.48 (COOH).

3,3-Diphenylacryloyl Chloride. The preceding acid (4.55 g, 0.020 mol) was dissolved in 10 mL of thionyl chloride. After the initial vigorous reaction, the mixture was stirred for 2 days at room temperature and then was placed under a 10^{-3} mm vacuum to remove HCl and SO$_2$. Distillation caused decomposition: ^{1}H NMR (CDCl$_3$) δ 5.84 (s, 1 H, =CH), 7.08−7.51 (m, 10 H, Ph); ^{13}C NMR (CDCl$_3$) δ 117.56 (=CH), 125.44, 127.92, 129.73, 131.06, 133.36 (Ph CH), 139.18, 141.38 (Ph ipso), 158.38 (Ph$_2$C=), 163.01 (COCl).

Reaction of 3,3-Diphenylacryloyl Chloride with (Me$_3$-Si)$_3$SiLi·CuI. Preparation of 1. To the (Me$_3$Si)$_3$SiLi formed from the treatment of 6.16 g (0.019 mol) of (Me$_3$Si)$_4$Si in 75 mL of THF with 16 mL of 1.5 M MeLi in ether overnight was added, at −78 °C, 3.62 g (0.019 mol) of CuI. The color of the reaction mixture changed from yellow to black. After the mixture was stirred for 1 h at −78 °C, 4.30 g (0.019 mol) of diphenylacryloyl chloride was added, and stirring was continued for 4 h before the reaction mixture was quenched in saturated ammonium chloride, followed by extraction with pentane. After removal of the solvent, Kugelrohr distillation at 180 °C/10^{-3} mm gave 3.84 g (47%) of red viscous liquid **1**: ^{1}H NMR (CDCl$_3$) δ 0.25 (s, 27 H, Me$_3$Si), 6.41 (s, 1 H, CH=), 6.99−7.60 (m, 10 H, Ph); ^{13}C NMR (CDCl$_3$) δ 1.84 (Me$_3$Si), 119.66 (=CHCO), 128.23, 128.90, 129.37, 130.07, 130.67 (Ph CH), 142.17, 144.97 (Ph ipso), 155.02 (Ph$_2$C=), 235.86 (Si*C*O); ^{29}Si NMR (CDCl$_3$) δ −70.92 (central Si), −11.33 (Me$_3$Si); MS *m/z* (EI) 455 (MH$^+$, 22), 439 (M$^+$ − Me, 12), 247 ((Me$_3$Si)$_3$Si$^+$, 11), 207 (Ph$_2$C=CHCO$^+$, 73).

Synthesis of (Me$_3$Si)$_3$SiCOCH=CMe$_2$ (2). To the (Me$_3$-Si)$_3$SiLi prepared from 5.91 g (0.018 mol) of (Me$_3$Si)$_4$Si in 75 mL of THF with 12 mL of 1.4 M MeLi in ether was added 3.43 g (0.018 mol) of CuI at −78 °C. The yellow solution changed to black. After 1 h of stirring at −78 °C, 2.13 g (0.018 mol) of 3,3-dimethylacryloyl chloride in 5 mL of THF was added. The mixture was allowed to warm to room temperature and was stirred overnight. After quenching with saturated ammonium chloride solution and extraction with pentane, the product was isolated by Kugelrohr distillation at 95 °C/10^{-3} mm, giving 4.93 g (83%) as a yellow liquid. **2**: ^{1}H NMR (CDCl$_3$) δ 0.21 (s, 27 H, Me$_3$Si), 1.81 (d, $^4J_{HH}$ = 1.4 Hz, Me *trans* to C=O), 1.98 (d, $^4J_{HH}$ = 1.18 Hz, Me *cis* to C=O), 6.35 (m, 1 H, CH=C); ^{13}C NMR (CDCl$_3$) δ 1.57 (Me$_3$Si), 20.97, 27.36 (each Me), 133.47 (*C*H=C), 145.33 (CH=*C*), 236.30 (C=O); ^{29}Si NMR (C$_6$D$_6$) δ −11.88 (Me$_3$Si), −72.60 (central Si); MS (*m/z* (EI) 315 (M$^+$ − Me, 52), 247 ((Me$_3$Si)$_3$Si$^+$, 11), 83 (Me$_2$C=CHCO$^+$, 45), 73 (Me$_3$Si, 100), 55 (Me$_2$C=CH$^+$, 16); IR (neat) 1639 (C=O), 1627 cm^{-1} (C=C−C=O).

Preparation of Me$_3$CCH=CHCOCl. 4,4-Dimethylpenten-2-oic acid was prepared in 26% yield from pivaldehyde and

Table 2. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters for 9[a]

empirical formula	C$_{23}$H$_{62}$OSi$_8$
M_r	579.5
crystal size (mm)	0.23 × 0.34 × 0.28
crystal class	triclinic
space group	$P\bar{1}$
temperature (K)	173
a (Å)	9.074(8)
b (Å)	24.002(8)
c (Å)	35.180(14)
α (deg)	104.65(3)
β (deg)	97.75(4)
γ (deg)	94.58(4)
V (Å^3)	7800(8)
Z	8
D_{calc} (g cm^{-3})	0.987
m(Mo Kα) (cm^{-1})	9.87
F(000)	2560
ω scan width (deg)	0.57
range θ collected (deg)	1−22.5 (±h,±k,l)
no. reflections collected	19770
independent reflections	18344
R_{int}	0.0486
no. observed data [$I > 2\sigma(I)$]	10143
R_1 [$I > 2\sigma(I)$]	0.0702
wR_2 (all data)	0.2237
goodness of fit	1.038
parameters refined	1175
max density in ΔF map (e/Å^3)	0.54

[a] Definition of R indices: $R_1 = \sum(F_o − F_c)/\sum(F_o)$; $wR_2 = [\sum[w(F_o^2 − F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

malonic acid:[9] ^{1}H NMR (CDCl$_3$) δ 0.91 (s, 9 H, Me$_3$C), 5.56 (d, $^3J_{HH}$ = 15.8 Hz, 1 H, =CHC=O), 6.88 (d, 1 H, Me$_3$CCH=C), 10.20 (br, 1 H, COOH); ^{13}C NMR (CDCl$_3$) δ 28.77 (*Me*$_3$C), 37.00 (Me$_3$*C*), 116.73 (=*C*HCO), 161.44 (Me$_3$C*C*H=), 172.26 (COOH). A 1.58 g (0.012 mol) sample of the acid was dissolved in 7 mL of SOCl$_2$ to form the acid chloride, 4,4-dimethylpenten-2-oyl chloride. After initial vigorous reaction, the mixture was stirred overnight and then distilled under vacuum to yield 1.56 g (96%) of colorless liquid: bp 25−30 °C/10^{-1} mm; ^{1}H NMR (CDCl$_3$) δ 1.10 (s, 9 H, Me$_3$C), 5.95 (d, $^3J_{HH}$ = 15.4 Hz, 1 H, =CHCO), 7.15 (d, 1 H, =CHCMe$_3$).

Preparation of (Me$_3$Si)$_3$SiCOCH=CHCMe$_3$ (3). To the (Me$_3$Si)$_3$SiLi prepared from 3.3 g (0.01 mol) of (Me$_3$Si)$_4$Si and 13.2 mL of a 1.4 M solution of methyllithium in ether was added 1.92 g (0.01 mol) of CuI at −78 °C. The color of the reaction mixture changed from yellow to black. After 1 h of stirring at −78 °C, 1.53 g of the acid chloride dissolved in 4 mL of THF was added all at once. The mixture was allowed to warm up to room temperature and was stirred for 2 days. Workup by quenching with saturated ammonium chloride solution followed by extraction with pentane gave, after removal of the solvents, a yellow liquid. Attempted purification by chromatography on silica gel or Kugelrohr distillation failed to significantly improve the unstable acylsilane beyond about 80% purity, but it was possible to assign the chemical shifts of the NMR spectra: ^{1}H NMR (CDCl$_3$) δ 0.20 (s, 27 H, Me$_3$Si), 1.04 (s, 9 H, Me$_3$C), 6.20 (s, $^3J_{HH}$ = 15.8 Hz, 1 H, =CHCO), 6.47 (d, 1 H, Me$_3$CCH=C); ^{13}C NMR (CDCl$_3$) δ 1.76 (Me$_3$Si), 29.37 (*Me*$_3$C), 32.05 (Me$_3$*C*), 134.10 (CO*C*H=C), 153.37 (Me$_3$C*C*=C), 235.00 (COSi); ^{29}Si NMR (CDCl$_3$) δ −72.69 (central Si), −11.80 (Me$_3$Si).

Preparation of Is(Me$_3$Si)$_2$SiCOCH=CMe$_2$ (4). To the [(2,4,6-triisopropylphenyl)bis(trimethylsilyl)silyl]lithium prepared from 4.0 g (0.0089 mol) of (Me$_3$Si)$_3$SiC$_{15}$H$_{23}$ (Is = C$_{15}$H$_{23}$) in 50 mL of THF and 10 mL of 1.4 M MeLi in ether at −78 °C was added 1.71 g (0.009 mol) of CuI in one portion. After 30 min of stirring, 1.05 g (0.0089 mol) of 3,3-dimethylacryloyl chloride (Aldrich) in 5 mL of THF was added. After 1 h of

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Table 3.   Bond Lengths (Å) and Angles (deg) for 1

Si(1A)−C(1A)	1.885(8)	Si(1A)−Si(3A)	2.348(4)
Si(1A)−Si(2A)	2.355(3)	Si(1A)−H1(SI)	1.23(6)
Si(2A)−C(7A)	1.847(10)	Si(2A)−C(6A)	1.849(10)
Si(2A)−C(8A)	1.857(9)	Si(3A)−C(10A)	1.842(10)
Si(3A)−C(11A)	1.868(9)	Si(3A)−C(9A)	1.871(10)
Si(4A)−O(1A)	1.658(6)	Si(4A)−C(14A)	1.858(9)
Si(4A)−C(13A)	1.861(9)	Si(4A)−C(12A)	1.864(9)
Si(5A)−C(3A)	1.938(8)	Si(5A)−Si(7A)	2.353(4)
Si(5A)−Si(6A)	2.357(4)	Si(5A)−Si(8A)	2.369(3)
Si(6A)−C(15A)	1.852(10)	Si(6A)−C(16A)	1.875(10)
Si(6A)−C(17A)	1.881(10)	Si(7A)−C(19A)	1.860(10)
Si(7A)−C(20A)	1.889(9)	Si(7A)−C(18A)	1.895(9)
Si(8A)−C(23A)	1.868(9)	Si(8A)−C(22A)	1.869(10)
Si(8A)−C(21A)	1.890(10)	O(1A)−C(1A)	1.408(9)
C(1A)−C(2A)	1.324(11)	C(2A)−C(3A)	1.509(10)
C(3A)−C(5A)	1.510(11)	C(3A)−C(4A)	1.550(11)
C(1A)−Si(1A)−Si(3A)	114.0(3)	C(1A)−Si(1A)−Si(2A)	116.8(3)
Si(3A)−Si(1A)−Si(2A)	114.12(13)	C(7A)−Si(2A)−C(6A)	111.5(5)
C(7A)−Si(2A)−C(8A)	108.5(5)	C(6A)−Si(2A)−C(8A)	108.6(5)
C(7A)−Si(2A)−Si(1A)	106.8(4)	C(6A)−Si(2A)−Si(1A)	110.8(3)
C(8A)−Si(2A)−Si(1A)	110.7(3)	C(10A)−Si(3A)−C(11A)	108.1(5)
C(10A)−Si(3A)−C(9A)	111.4(5)	C(11A)−Si(3A)−C(9A)	109.3(5)
C(10A)−Si(3A)−Si(1A)	114.7(4)	C(11A)−Si(3A)−Si(1A)	105.3(3)
C(9A)−Si(3A)−Si(1A)	107.7(4)	O(1A)−Si(4A)−C(14A)	109.2(4)
O(1A)−Si(4A)−C(13A)	111.1(4)	C(14A)−Si(4A)−C(13A)	112.8(4)
O(1A)−Si(4A)−C(12A)	104.6(4)	C(14A)−Si(4A)−C(12A)	111.1(4)
C(13A)−Si(4A)−C(12A)	107.7(4)	C(3A)−Si(5A)−Si(7A)	112.0(3)
C(3A)−Si(5A)−Si(6A)	111.4(3)	Si(7A)−Si(5A)−Si(6A)	107.99(13)
C(3A)−Si(5A)−Si(8A)	110.9(3)	Si(7A)−Si(5A)−Si(8A)	106.78(13)
Si(6A)−Si(5A)−Si(8A)	107.62(14)	C(15A)−Si(6A)−C(16A)	105.5(5)
C(15A)−Si(6A)−C(17A)	108.5(5)	C(16A)−Si(6A)−C(17A)	109.1(5)
C(15A)−Si(6A)−Si(5A)	112.2(4)	C(16A)−Si(6A)−Si(5A)	110.3(3)
C(17A)−Si(6A)−Si(5A)	111.1(3)	C(19A)−Si(7A)−C(20A)	107.1(5)
C(19A)−Si(7A)−C(18A)	107.3(5)	C(20A)−Si(7A)−C(18A)	106.8(5)
C(19A)−Si(7A)−Si(5A)	112.7(4)	C(20A)−Si(7A)−Si(5A)	110.2(3)
C(18A)−Si(7A)−Si(5A)	112.4(3)	C(23A)−Si(8A)−C(22A)	107.1(5)
C(23A)−Si(8A)−C(21A)	106.3(5)	C(22A)−Si(8A)−C(21A)	108.7(5)
C(23A)−Si(8A)−Si(5A)	109.6(3)	C(22A)−Si(8A)−Si(5A)	111.9(3)
C(21A)−Si(8A)−Si(5A)	112.8(3)	C(1A)−O(1A)−Si(4A)	130.5(5)
C(2A)−C(1A)−O(1A)	119.7(7)	C(2A)−C(1A)−Si(1A)	124.8(6)
O(1A)−C(1A)−Si(1A)	115.5(6)	C(1A)−C(2A)−C(3A)	134.4(8)
C(2A)−C(3A)−C(5A)	114.8(7)	C(2A)−C(3A)−C(4A)	105.1(7)
C(5A)−C(3A)−C(4A)	107.5(7)	C(2A)−C(3A)−Si(5A)	110.3(5)
C(5A)−C(3A)−Si(5A)	110.0(5)	C(4A)−C(3A)−Si(5A)	108.8(6)

stirring at −78 °C, the reaction mixture was allowed to warm to room temperature, quenched with saturated NH$_4$Cl solution, extracted with hexane, and purified by chromatography on silica gel using hexane as eluent to yield 1.4 g (35%) of golden colored liquid **4**: ^{1}H NMR (CDCl$_3$) δ 0.23 (s, 18 H, Me$_3$Si), 1.18 (d $^3J_{HH}$ = 6.6 Hz, 12 H, o-CH*Me*$_2$), 1.26 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, p-CHMe$_2$), 1.76 (d, $^4J_{HH}$ = 1.0 Hz, 3 H, Me), 2.09 (d, $^4J_{HH}$ = 1.1 Hz, 3 H, Me), 2.87 (sept, 1 H, p-C*H*Me$_2$), 2.97 (sept, 2 H, o-C*H*Me$_2$), 6.38 (m, I H, CH=), 7.00 (s, 2 H, CH arom); ^{13}C NMR (CDCl$_3$, APT) δ 1.11 (Me$_3$Si), 20.97, 27.18 (each MeC=C), 23.81 (p-CH*Me*$_2$), 25.62 (o-CH*Me*$_2$), 33.91 (p-*C*HMe$_2$), 35.98 (o-*C*HMe$_2$), 121.54 (CH arom), 127.54 (ipso arom), 130.62 (*C*H=C), 147.13 (Me$_2$*C*=C), 149.39, 155.86 (each *C*-i-Pr), 236.26 (C=O); ^{29}Si NMR (CDCl$_3$) δ −44.41 (central Si), −13.58 (Me$_3$Si); MS m/z (EI) 461 (M$^+$ + H, 4), 387 (M$^+$ − Me$_3$Si, 24), 73 (Me$_3$Si$^+$, 100); IR (neat) 1632 (C=O), 1605 cm^{-1} (C=C).

Preparation of Is(Me$_3$Si)$_2$SiCOCH=CPh$_2$ (5). To the silyl cuprate reagent prepared as described was added, at −78 °C over 20 min, 1 equiv of 3,3-diphenylacryloyl chloride in 20 mL of THF. After warming to room temperature, quenching with ammonium chloride solution, and purification by chromatography on silica gel using hexane as eluent, a 17% yield of an unstable red liquid, Is(Me$_3$Si)$_2$SiCOCH=CPh$_2$ (**5**), was obtained: ^{1}H NMR (CDCl$_3$) δ 0.24 (s, 18 H, Me$_3$Si), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6 H, p-CH*Me*$_2$), 1.27 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, o-CH*Me*$_2$), 2.89 (sept, 1 H, p-C*H*Me$_2$), 3.02 (sept, 2 H, o-C*H*Me$_2$), 6.42 (s, 1 H, CH=C), 6.97−7.36 (m, 12 H, CH arom); ^{13}C NMR δ 0.84 (Me$_3$Si), 23.86 (p-CH*Me*$_2$), 25.71 (o-CH*Me*$_2$), 34.15 (p-*C*HMe$_2$), 36.20 (o-*C*HMe$_2$), 121.13 (*C*H=C), 155.86 (Ph$_2$*C*=C), 121.46 (CH of Is), 127.36 (C ipso of Is), 127.86,

128.19, 128.57, 129.65, 128.83 (CH arom), 138.87, 141.92 (C ipso of Ph), 146.23, 149.63 (C quat of Is), 232.56 (C=O); ^{29}Si NMR (CDCl$_3$) δ −43.07 (central Si), −13.52 (Me$_3$Si).

Preparation of Mes$_2$C=CHCOCl. 1,1-Dimesitylethylene (Mes$_2$C=CH$_2$) was prepared in low yield as described from acetomesitylene and polyphosphoric acid:[10] ^{1}H NMR (CDCl$_3$) δ 2.17 (s, 12 H, o-Me), 2.28 (s, 6 H, p-Me), 5.54 (s, 2 H, =CH$_2$), 6.86 (s, 4 H, CH arom); ^{13}C NMR (CDCl$_3$) δ 21.38 (p-Me), 22.00 (o-Me), 124.84 (=CH$_2$), 129.93 (CH arom), 136.50 (C ipso), 136.93 (o-C quat), 139.05 (p-C quat), 144.40 (Mes$_2$C=).

Mes$_2$C=CHBr. To a solution of 7.62 g (0.029 mol) of 1,1-dimesitylethylene in 200 mL of glacial acetic acid was added 4.63 g (0.023 mol) of bromine. After stirring for 2 h, the mixture was diluted with 200 mL of hexanes and washed three times with distilled water. Half the hexanes were removed under reduced pressure, and the residue, left at 0 °C overnight, deposited 8.49 g (85%) of crystals of Mes$_2$C=CHBr: mp 105−106 °C; ^{1}H NMR (CDCl$_3$) δ 2.18 (s, 12 H, o-Me), 2.26 (s, 6 H, p-Me), 6.46 (s, 1 H, CHBr=), 6.85 (s, 4 H, CH arom); ^{13}C NMR (CDCl$_3$): δ 21.41, 21.50 (each o-Me), 21.58, 22.30 (each p-Me), 113.34 (=CHBr), 129.48, 130.50 (CH arom), 135.74, 136.81 (C ipso), 137.52, 137.60 (o-C quat), 137.97, 142.87 (p-C quat). Anal. Calcd for C$_{20}$H$_{23}$Br: C, 69.97; H, 6.70. Found: C, 69.79; H, 6.66.

To a solution of 10.68 g (0.031 mol) of the bromide in 100 mL of THF at −78 °C was added 20 mL of 2.4 M n-butyllithium in hexane. The mixture was stirred for 2 h and then carbonated. Workup with dilute acid, extraction with ether, and

(10) Snyder, H. R.; Roiske, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 5820.

removal of the ether yielded 8.16 g (85%) of the acid Mes$_2$C=CHCOOH after recrystallization from methanol: mp 189−190 °C; ^{1}H NMR (CDCl$_3$) δ 2.11 (s, 12 H, *o*-Me), 2.26 (s, 6 H, *p*-Me), 6.08 (s, 1 H, =CH), 6.80 (s, 4 H, CH arom); ^{13}C NMR (CDCl$_3$) δ 21.30 (*o*-Me), 21.49 (*p*-Me), 126.04 (CH=), 129.46, 130.50 (CH arom), 135.72 (C ipso), 137.18, 137.48, 138.15 (*C*-Me arom), 155.30 (Mes$_2$*C*=), 171.55 (COOH); MS *m*/*z* (EI) 308 (M$^+$, 48), 293 (M$^+$ − Me, 68), 234 (100), 119 (C$_9$H$_{11}^+$, 21). Anal. Calcd for C$_{21}$H$_{24}$O$_2$: C, 81.82; H, 7.79. Found: C, 81.75; H, 7.94. The acid (2.20 g, 0.007 mol) was dissolved in 10 mL of thionyl chloride to form Mes$_2$C=CHCOCl. The reaction mixture was stirred for 3 days and then the excess SOCl$_2$ was removed under vacuum: ^{1}H NMR (CDCl$_3$) δ 2.19 (s, 12 H, *o*-Me), 2.33 (s, 6 H, *p*-Me), 6.44 (s, 1 H, =CH), 6.89 (s, 4 H, CH arom); ^{13}C NMR (CDCl$_3$) δ 21.20, 21.49, 21.64 (Me of Mes), 129.83, 130.62 (CH arom), 130.92 (=CH), 134.61, 136.40 (C ipso), 137.22, 138.92, 139.33 (C-Me quat), 158.47 (Mes$_2$C=), 163.30 (COCl).

Attempted Coupling of 3,3-Dimesitylacryloyl Chloride with [Tris(trimethylsilyl)silyl]Lithium·CuI. Formation of Mes$_2$C=CHCOCOCH=CMes$_2$. To the silyllithium cuprate prepared from 2.33 g (0.0071 mol) of (Me$_3$Si)$_4$Si was added, at −78 °C, 2.29 g of the acid chloride in 30 mL of THF. The color immediately changed to red-black. The mixture was stirred for 2 h, quenched with NH$_4$Cl solution, and extracted with hexane. Chromatography on silica gel led to the isolation of 1.02 g (50%) of 1,1,6,6-tetramesityl-3,4-dioxohexa-1,5-diene as orange crystals: mp 125−126 °C; ^{1}H NMR (CDCl$_3$) δ 1.86, 2.09, 2.26, 2.27 (s, Me), 6.24 (s, 2 H, C=CH), 6.83 (br s, 8 H, CH arom); ^{13}C NMR (CDCl$_3$) δ 21.33, 21.41, 29.90 (Me), 129.81, 130.53 (CH arom), 136.12 (C ipso), 136.87 (*C*H=), 137.46, 137.67, 138.01, 138.46 (Me-*C* arom), 150.34 (Mes$_2$*C*=C), 201.41 (C=O); IR (Nujol) 1666, 1603, 1581 cm^{-1}; MS *m*/*z* (EI) 291 (M$^+$/2, 100), 119 (Mes$^+$, 4). Anal. Calcd for C$_{42}$H$_{26}$O$_2$: C, 86.56; H, 7.95. Found: C, 86.33; H, 8.65. The ^{13}C NMR and ^{29}Si NMR spectra of the crude reaction mixture prior to chromatography suggested the presence of some (Me$_3$Si)$_3$SiCO-CH=CMes$_2$ [^{13}C NMR (C$_6$D$_6$) δ 234.16 (SiC=O); ^{29}Si NMR (C$_6$D$_6$) δ −72.6 (central Si), −11.88 (Me$_3$Si)]. However, the compound did not survive the chromatography.

Thermolysis of (Me$_3$Si)$_3$SiCOCH=CMe$_2$ (2). Formation of Compound 9. A 3.06 g (0.011 mol) sample of (Me$_3$-Si)$_3$SiCOCH=CMe$_2$ was heated in an oil bath at 130 °C under 10^{-3} mm vacuum for 30 min. A low-boiling material was collected, and the residue was recrystallized from acetone to yield 1.75 g (56%) of **9**: mp 75−76 °C; ^{1}H NMR (CDCl$_3$) δ 0.21, 0.24 (each s, 27 H, (Me$_3$Si)$_3$Si), 1.40 (s, 6 H, Me), 3.52 (s, 1 H, SiH), 4.71 (s, 1 H, =CH); ^{13}C NMR (CDCl$_3$) (APT) δ 0.59 ((*Me$_3$-Si*)$_2$SiH), 1.73 (OSiMe$_3$), 2.54 ((*Me$_3$Si*)$_3$Si), 30.15 (Me$_2$*C*), 31.36 (*Me$_2$*C), 136.08 (=CH), 145.19 (=*C*OSiMe$_3$); ^{29}Si NMR (CDCl$_3$)

δ 14.45 (OSiMe$_3$), −13.36 ((Me$_3$*Si*)$_3$Si), −14.88 ((Me$_3$*Si*)$_2$SiH), −61.07 ((Me$_3$Si)$_3$*Si*), −62.62 (d, $^1J_{Si-H}$ = 154.8 Hz, (Me$_3$-Si)$_2$*SiH*); MS *m*/*z* (EI) 563 (M − Me, 1), 331 (M$^+$ − (Me$_3$Si)$_3$Si, 43), 247 ((Me$_3$Si)$_3$Si, 8), 243 (29), 175 ((Me$_3$Si)$_2$SiH$^+$, 11), 174 ((Me$_3$Si)$_2$Si$^+$, 10), 173 ((Me$_3$Si)$_3$Si$^+$ − Me$_3$SiH, 28), 73 (Me$_3$Si$^+$, 100). The lower boiling fraction was shown to be (Me$_3$-Si)$_3$SiH: 0.3 g (11%); ^{13}C NMR (CDCl$_3$) δ 2.29 (Me$_3$Si); ^{29}Si NMR (CDCl$_3$) δ −11.38 (s, Me$_3$Si), −115.07 (Si central); IR (neat) 2087.5 cm^{-1} (SiH).

X-ray Structural Determination. A summary of selected crystallographic data is given in Table 2. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The intensities of three standard reflections measured every 97 reflections showed no decay. The data were corrected for Lorenz and polarization effects and for absorption.[11] Minimum and maximum absorption corrections were 0.6380 and 0.9868.

The structures were solved and refined by using the SHELXTL/PC[12] package. Refinement was by full-matrix least squares on F^2 using all data. The weighting scheme was w = $1/[\sigma^2(F_o^2) + (0.084P)^2 + 21.44P]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms.

With Z = 8 in the space group $P\bar{1}$, there are four independent molecules in the asymmetric unit. Each molecule is chemically identical, and there are no significant differences in the geometries of the molecules. However, in one of the molecules there is a rotational disorder about the C−Si(SiMe$_3$) bond, so that the minor disorder component has SiMe$_3$ rotated by approximately 32° relative to the major component. The relative occupancies of the minor and major components are 0.11 and 0.89. Only the Si atoms of the minor component were located. Relevant bond lengths and angles of **9** are given in Table 3. Figure 1 shows the structure.

Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and hydrogen atom coordinates for compound **9** (17 pages). Ordering information is given on any current masthead page.

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